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NH AND OH CONCENTRATION PROFILES IN A STOICHIOMETRIC CH<sub>4</sub>/N<sub>2</sub>O FLAME BY LAS. (U) ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND ABERDEEN PROVI.

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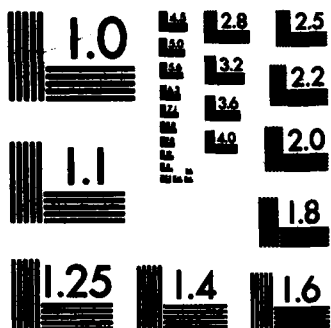
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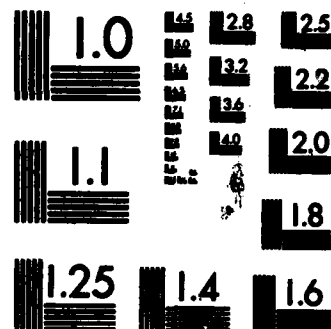
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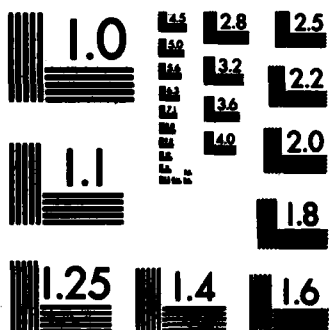
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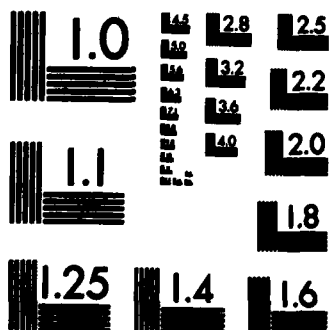
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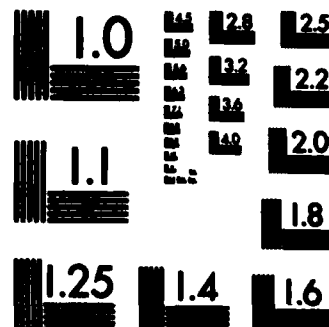
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TECHNICAL REPORT ARBRL-TR-02426

NH AND OH CONCENTRATION PROFILES IN A  
STOICHIOMETRIC  $\text{CH}_4/\text{N}_2\text{O}$  FLAME BY LASER  
EXCITED FLUORESCENCE AND  
ABSORPTION TECHNIQUES

William R. Anderson  
Leon J. Decker  
Anthony J. Kotlar

October 1982

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  The concentration profiles of NH and OH were measured in an atmospheric pressure premixed laminar CH <sub>4</sub> /N <sub>2</sub> O flame over a porous plug flat flame burner. Relative profiles were obtained by laser excited fluorescence for both compounds and normalized by laser absorption at a single point for NH. The OH concentration was high enough to allow absorption measurements at several points for comparison with fluorescence results. The steeply rising portions of the profiles occur at about the same height above the burner but		

## Abstract Cont'd.

20. the NH is confined to the primary reaction zone while the OH decay extends into the burnt gases. The apparent OH decay was found, using a simple analysis, to be consistent with second order kinetics as observed by previous workers on other flames. However, it should be noted that diffusion of OH is at least partially responsible for the apparent shape of the profile resulting in the second order decay kinetics found using the simple analysis. The decay rate is smaller than that observed by previous workers for CH<sub>4</sub>/air flames. Qualitative reasons for the different decay rates found in the studies are discussed in detail. A strong dependence of OH decay rate on final flame temperature, and hence the cooling rate peculiar to the burner used in any particular study, is predicted. Brief studies of the peak NH concentration in CH<sub>4</sub>/air, CH<sub>4</sub>/NO, H<sub>2</sub>/NO, and H<sub>2</sub>/N<sub>2</sub>O flames were made in order to elucidate the flame chemistry.

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## I. INTRODUCTION

In the determination of chemical flame mechanisms, highly spatially resolved concentration measurements of reactive trace species are very important for comparison with flame models. Mass spectrometry and other techniques involving physical extraction of a sample from flames have been widely applied but may affect the concentration through perturbation of the flame by a probe or by reactions within the probe.<sup>1-4</sup> Spectroscopic techniques involving discharge or lamp sources do not intrude upon the flame but usually do not provide enough spatial resolution and sensitivity. Recently, laser based techniques, such as laser absorption for more prominent species and laser excited fluorescence have received considerable attention.<sup>5,6</sup> Both techniques have been applied for highly spatially resolved temperature measurement using the OH radical (see Ref. 7 and references therein). Radical concentration profiles have been measured using laser absorption by Luck and coworkers<sup>8</sup>, Cattolica and

<sup>1</sup>Revet, J.M., Peuchberty, D. and Cottureau, M.J., "A Direct Comparison of Hydroxyl Concentration Profiles Measured in a Low Pressure Flame by Molecular Beam Mass Spectrometry and Ultraviolet Absorption Spectroscopy," Combustion and Flame, Vol. 33, p. 5, 1978.

<sup>2</sup>Cattolica, R.J., Yoon, S. and Knuth, E.L., "OH Concentration in an Atmospheric-Pressure Methane-Air Flame from Molecular-Beam Mass Spectrometry and Laser-Absorption Spectroscopy," Paper 80-44, Western Section Fall Meeting of the Combustion Institute, Los Angeles, California, October, 1980.

✓ <sup>3</sup>Eckbreth, A.C. and Hall, R.J., "CARS Concentration Sensitivity With and Without Nonresonant Background Suppression," Combustion Science Tech., Vol. 25, p. 175, 1981.

<sup>4</sup>Johnson, G.M., Smith, M.Y. and Mulcahy, M.F.R., "The Presence of NO<sub>2</sub> in Premixed Flames," Seventeenth Symposium (Int.) on Combustion, The Combustion Institute, p. 647, Pittsburgh, PA, 1979.

<sup>5</sup>Crosley, D.R., Ed., "Laser Probes for Combustion Chemistry," ACS Symposium Series 134, American Chemical Society, Washington, D.C., 1980.

<sup>6</sup>Hastie, J.W., Ed., "Characterization of High Temperature Vapors and Gases," Proceedings of the 10th Materials Research Symposium, Gaithersburg, MD, National Bureau of Standards Special Publication 561/2, U.S. Government Printing Office, Washington, D.C., Vol. II, Section VI, 1979.

<sup>7</sup>Anderson, W.R., Decker, L.J. and Kotlar, A.J., "Temperature Profile of a Stoichiometric CH<sub>4</sub>/N<sub>2</sub>O Flame from Laser Excited Fluorescence Measurements on OH, to appear in Combustion and Flame.

✓ <sup>8</sup>a. Lück, K.C. and Thielen, W., "Measurements of Temperatures and OH Concentrations in a Lean Methane-Air Flame Using High-Resolution Laser-Absorption Spectroscopy," J. Quant. Spectrosc. Radiat. Transfer, Vol. 20, p. 71, 1978. b. Luck, K.C., and Tsatsaronis, G., "A Study of Flat Methane-Air Flames at Various Equivalence Ratios," Acta Astronautica, Vol. 6 p. 467, 1979. c. Lück, K.C., "Hochauflösende Laserabsorptionsspektroskopie zur Temperatur- und Konzentrationsbestimmung in Laminaren Flammen," Dissertation, TH Aachen, 1977.

coworkers<sup>2,9</sup> and by Green.<sup>10</sup> Laser fluorescence has been used for profiling by Muller, Schofield and Steinberg<sup>11</sup>, by Bechtel and Teets<sup>12</sup> and by Cottureau and Stepowski<sup>13</sup>. Of these, the flame front itself was probed only in the work involving low pressure flames by Green, and by Cottureau and Stepowski, and at atmospheric pressure by Bechtel and Teets using a burner which produces a curved flame that is vertically cooled.

In the present work, concentration profiles of NH and OH in a stoichiometric CH<sub>4</sub>/N<sub>2</sub>O flame were measured by a combination of laser fluorescence and absorption techniques applied to the NH A<sup>3</sup>Π + X<sup>3</sup>Σ<sup>-</sup> and the OH A<sup>2</sup>Σ<sup>+</sup> + X<sup>2</sup>Π systems. The concentration measurements extend well into the flame front over a sintered-porous-plug, flat-flame burner. The apparent OH decay was consistent, within experimental error, with a second order decay law as observed previously in H<sub>2</sub>/air<sup>14,15</sup> and CH<sub>4</sub>/air<sup>8,9,16</sup> flames. Other studies on H<sub>2</sub>/O<sub>2</sub>/inert diluent

<sup>9</sup> Cattolica, R.J., "Laser Absorption Measurements of OH in a Methane-Air Flat Flame," paper 79-54, Western Section Fall Meeting of the Combustion Institute, Berkeley, CA, October, 1979.

<sup>10</sup> Green, R.M. and Miller, J.A., "The Measurement of Relative Concentration Profiles of NH<sub>2</sub> Using Laser Absorption Spectroscopy," Sandia Report No. SAND80-8858, submitted for publication.

<sup>11</sup> Muller, III, C.H., Schofield, K. and Steinberg, M., "Laser Induced Fluorescence Spectroscopy Applied to Hydroxyl in Flames," in Ref. 5, p. 103.

<sup>12</sup> Bechtel, J.H. and Teets, R.E., "Hydroxyl and Its Concentration Profile in Methane-Air Flames," Appl. Opt., Vol. 18, p. 4138, 1979.

<sup>13</sup> a. Cottureau, M.J. and Stepowski, D., "Laser Induced Fluorescence Spectroscopy Applied to Hydroxyl in Flames," in Ref. 5, p. 131. b. Stepowski, D., and Cottureau, M.J., "Study of the Collisional Lifetimes of Hydroxyl (<sup>2</sup>Σ<sup>+</sup>, v' = 0) Radicals in Flames by Time Resolved Laser Induced Fluorescence," Combustion and Flame, Vol. 40, p. 65, 1981.

<sup>14</sup> Bulewicz, E.M., James, C.G. and Sugden, T.M., "Photometric Investigations of Alkali Metals in Hydrogen Flame Gases II. The Study of Excess Concentrations of Hydrogen Atoms in Burnt Gas Mixtures," Proc. Roy. Soc., Vol. A235, p. 89, 1956.

<sup>15</sup> a. Kaskan, W.E., "Hydroxyl Concentrations in Rich Hydrogen-Air Flames Held on Porous Burners," Combustion and Flame, Vol. 2, p. 229, 1958. b. Kaskan, W.E., "The Concentration of Hydroxyl and of Oxygen Atoms in Gases from Lean Hydrogen-Air Flames," Combustion and Flame, Vol. 2, p. 286, 1958.

<sup>16</sup> Egorov, V.I., Ermolenko, V.I. and Ryabihov, O.B., "Measurement of Absolute Hydroxyl Concentrations Behind the Front of a Planar Flame of Methane-Air Mixtures," Doklady Akademii Nauk SSSR, Vol. 215, p. 370, 1974, English, 275.

mixtures<sup>17,18</sup> and a study of the effects of diffusion in the CH<sub>4</sub>/air flame<sup>9</sup> indicate that diffusion changes the apparent shape of the OH profile, resulting in the observed second order decay. The decay was slower in the CH<sub>4</sub>/N<sub>2</sub>O flame studies in this laboratory than in the previous studies on stoichiometric CH<sub>4</sub>/air<sup>8,9,16</sup>. Qualitative reasons for the difference will be discussed. A strong dependence of the decay rate on the final flame temperature is predicted. The decay rate will thus be strongly dependent on the heat extraction rate from the flame and hence, the burner design and possibly the reactant mixture flow rate. The effect has previously been discussed briefly elsewhere.<sup>19</sup>

In order to elucidate the flame chemistry the NH concentration was briefly studied, with less exacting measurements since the temperature was only estimated from water cooling rates, in CH<sub>4</sub>/air, H<sub>2</sub>/N<sub>2</sub>O, CH<sub>4</sub>/NO and H<sub>2</sub>/NO flames. The less precise measurements are adequate for our purposes. The measurements indicate the peak NH concentration in the N<sub>2</sub>O flames is about the same while no fluorescence of NH could be found in the other flames, indicating the concentration there is much lower. The peak concentration in the N<sub>2</sub>O flames is about 5 orders of magnitude higher than expected at equilibrium. The high concentration of NH is probably due, indirectly, to a bimolecular reaction resulting in the breakage of the N-N bond of the N<sub>2</sub>O. It is difficult at present to identify the formation reaction(s). A number of possibilities are discussed.

## II. EXPERIMENTAL

The experimental apparatus is identical to that used for temperature measurement in the CH<sub>4</sub>/N<sub>2</sub>O flame.<sup>7</sup> The apparatus will only be briefly discussed here. A pulsed, flashlamp pumped dye laser was focussed over a sintered-bronze, porous-plug burner supporting a CH<sub>4</sub>/N<sub>2</sub>O flame. The beam diameter at the burner center was approximately 200 $\mu$ . For absorption measurements on NH, an aperture was placed in the beam reducing the diameter at flame entry and exit points to about 200 $\mu$  as well. Pathlengths of course varied with position in the flame. They were all approximately 5-6 cm with error limits of 0.1 cm. Small portions of the beam were sampled by two photodiodes just prior to its entry and after its exit from the flame. Fluorescence was sampled by a 35 cm monochromator. The appropriate signals were ratioed in two boxcar averagers to obtain fluorescence and absorption spectra. Hard copy of the spectra was obtained on a strip chart recorder. For some of the OH absorption measurements, the boxcar outputs were directly digitized by a PDP 11/04 computer for later analysis of the lineshapes.

<sup>17</sup>Fenimore, C.P. and Jones, G.W., "Radical Recombination and Heat Evolution in H<sub>2</sub> - O<sub>2</sub> Flames," Tenth Symposium (Int.) on Combustion, The Combustion Institute, Pittsburg, PA, p. 489, 1965.

<sup>18</sup>Getzinger, R.W. and Schott, G.L., "Kinetic Studies of Hydroxyl Radicals in Shock Waves. V. Recombination via the H + O<sub>2</sub> + M  $\rightarrow$  HO<sub>2</sub> + M Reaction in Lean Hydrogen-Oxygen Mixtures," *J. Chem. Phys.*, Vol. 43, p. 3237, 1965.

<sup>19</sup>Anderson, W.R., Decker, L.J., and Kotlar, A.J., "Concentration Profiles of NH and OH in a Stoichiometric CH<sub>4</sub>/N<sub>2</sub>O Flame by Laser Excited Fluorescence and Absorption," to appear in *Combustion and Flame*.

For measurement of fluorescence concentration profiles, using the theory of geometric optics, it is easy to show that for the approximate point source above the center of the burner a portion of the lower half of the gathering lens is occluded from the source by the burner. As the burner height is changed, the amount of occlusion changes. To avoid complicated data reduction, the lower half of the lens was blocked by a piece of black paper in fluorescence concentration profiling measurements. The loss in signal was more than compensated by ease in data reduction.

### III. RESULTS

Relative fluorescence profile measurements were made by choosing one well-resolved transition from the spectrum of the radical of interest. The laser scanned this transition after each burner height change. Scanning was necessary since the amount of scattering from the burner head varies with height and, in fact, becomes a serious problem as the burner head is approached. The (0,0)  $R_{11}$  and the (1,1)  $R_{15}$  transitions were chosen for NH and OH profiling, respectively. For NH, the monochromator was set at the dense P-branch blend at 3372.5 Å with bandwidth 5 Å FWHM. These settings are similar to those used in the first laser fluorescence study in the A-X system of NH performed in a flow system in this laboratory<sup>20</sup>. For OH, the monochromator was set at 3175 Å with bandpass 36 Å. Line positions for NH were obtained from the work of Dixon<sup>21</sup> and for OH from the work of Dieke and Crosswhite<sup>22</sup>. Usage of the (1,1) band was necessary for OH in order to avoid laser beam depletion, since the concentration is quite high, as discussed in the temperature measurements of Ref. 7.

In retrospect, it would probably be better to use an NH rotational line having  $N''$ , the ground state rotational quantum number, equal to 5 or 6 which is nearer the peak in the rotational distribution for the temperature range of interest. Changes in the Boltzmann factor for these states are smaller than others and they are thus less temperature sensitive. Also, the R-branch transitions of  $N'' = 5$  or 6 are at wavelengths far enough removed from the Q-branch at 3360 Å that the monochromator might be set there without introducing too much scattering. This arrangement could improve the S/N ratio considerably. However, as will be seen, quite adequate results could be obtained using the (0,0)  $R_{11}$ . For OH, pumping occurs in the  $v'' = 1$  state whose population is rather temperature dependent. A line having  $N'' = 5$  was chosen since at least the rotational portion of the partition function exhibits little temperature sensitivity and large signal levels could be obtained.

<sup>20</sup>Anderson, W.R. and Crosley, D.R., "Laser Excited Fluorescence in the A-X System of NH," Chem. Phys. Lett., Vol. 62, p. 275, 1979.

<sup>21</sup>Dixon, R.N., "The (0,0) and (1,0) Bands of the  $A(^3\Pi_i) - X(^3\Sigma^-)$  System of NH," Can. J. Phys., Vol. 37, p. 1171, 1959.

<sup>22</sup>Dieke, G.H. and Crosswhite, H.M., "The Ultraviolet Bands of OH: Fundamental Data," J. Quant. Spectrosc. Radiat. Transfer, Vol. 2, p. 97, 1962.

The peakwidths were examined as a function of height above the burner and since no differences, within error limits, were found it was assumed that the relative intensities were proportional to peak heights. It was also assumed that the fluorescence yield, which is dependent on excited state quenching and rotational relaxation rates, is constant at all positions in the flame. This assumption will be discussed in more detail later.

For measurements very close to the burner surface, a portion of the laser beam hits the top of the burner and is lost for pumping purposes. Fig. 1 shows how the focussed beam interacts with the burner head, assuming refraction does not cause significant beam deflection. As was discussed in Ref. 7, the beam is deflected less than  $50\mu$  in traversing the flame even in the flame front region. As the beam propagates over the burner, its lower portion is first clipped by the front edge of the burner. The beam then passes through the fluorescence sampling region, i.e. the beam waist volume, where it is inverted due to the focussing. The lower portion of the inverted beam is then clipped further on the burner head as the beam expands. Owing to the symmetry of the clipping effect, one can readily see that the transmission across the burner head is related to the beam intensity in the sampling region by the equation

$$I_{BW} = I_T + \frac{1}{2} (I_0 - I_T) = \frac{1}{2} (I_0 + I_T) \quad (1)$$

where  $I_{BW}$  is the intensity at the beam waist,  $I_T$  the transmitted intensity and  $I_0$  the incident intensity. The  $I_T$  term represents the portion of the light seen by the transmission photodiode while the  $\frac{1}{2} (I_0 + I_T)$  term represents that portion of the light which is incident on the probe volume but screened from the diode by the burner due to the inversion of the beam.  $I_0$  was measured with the burner removed.  $I_T$  was measured for a given height when the laser wavelength was non-resonant with any transition. Fluorescent responses at heights affected by beam clipping were then normalized by  $I_{BW}$ .

For conversion of fluorescence intensity profiles to concentration profiles, the radicals were assumed to be in thermal equilibrium. For OH, the ground state was shown to be in rotational equilibrium in Ref. 7. Absorption measurements indicate the  $v'' = 0$  and 1 states are in equilibrium within experimental error as well. For NH, an R-branch excitation scan, discussed later in this paper, shows that it is also in rotational equilibrium. The density in the ground state  $v'', N'', J''$  is then given by

$$N_{v'', N'', J''} = \frac{(2J'' + 1) [X] \exp (-E_{v'', N'', J''}/kT)}{C Q_{vib} Q_{rot}} \quad (2)$$

where  $[X]$  is the concentration of radical  $X = \text{OH}$  or  $\text{NH}$ ,  $E_{v'', N'', J''}$  is the ground state energy,  $k$  is the Boltzmann constant,  $T$  the temperature,  $C$  is a factor accounting for spin splitting and lambda doubling in the ground electronic state ( $C = 3$  for  $\text{NH}$  and  $4$  for  $\text{OH}$ ) and  $Q_{vib}$  and  $Q_{rot}$  are the vibrational and rotational partition functions, respectively. The temperatures were estimated by interpolation of the results of Ref. 7. The necessary spectral constants were obtained from Ref. 21 and 22.

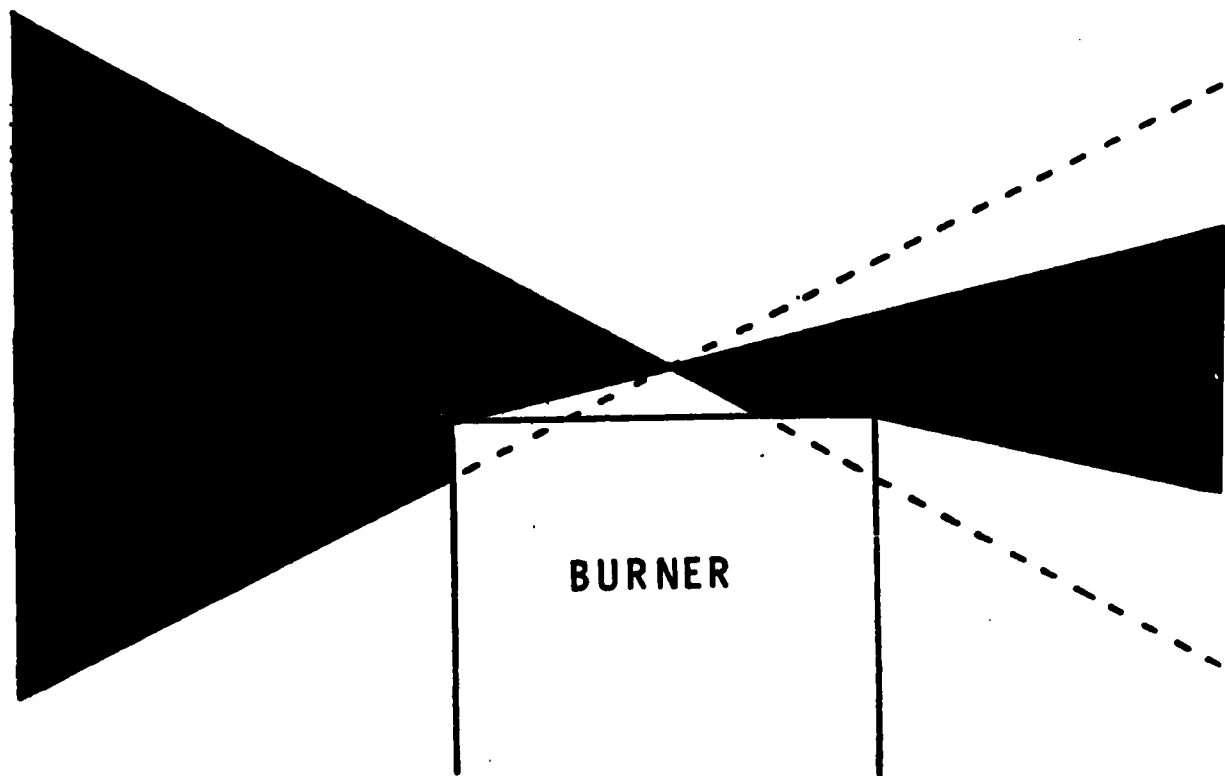


Fig. 1. Interaction of the focussed laser beam (dark area) with the burner head at small heights. The beam enters at the left and exits at the right. Point focussing is assumed for purposes of the discussion. The focussing angle is greatly exaggerated.

Relative density profiles were obtained using the fluorescence data and Eq. 2. (To reduce the data, it was assumed the fluorescence yield is proportional to ground state density. This assumption is discussed later). The profiles were then calibrated using absorption measurements. For OH, the absorption data were precise enough to allow comparison of profiles resulting from the two techniques. The computer program discussed in Ref. 7, which accounts for the laser linewidth, collisional and Doppler broadening, was used to extract the absolute concentration from the absorption line shapes. The resulting concentration profile using the two-line, curve-fitting approach is shown in Fig. 2. (Equivalent results were also obtained at 1.0 cm by fitting three lines in the absorption spectrum only, and by fitting five lines in the absorption and fluorescence spectra simultaneously in the manner discussed in Ref. 7). Error limits on the concentrations in Fig. 2 reflect only the precision limits of the fit. Some systematic error may result owing to nonuniformity of the flame (see Fig. 3, Ref. 7) and the line of sight nature of absorption measurements. The calibration for NH was performed at the peak of the concentration profile, 550 $\mu$  above the burner. A slightly higher absorption, and correspondingly higher number density, than previously reported<sup>23</sup> was observed with the apertured laser beam used in the present work. This result was expected since the NH profile, as will be seen, is sharply peaked. The largest NH absorption was only about 3% which is not enough to cause significant laser depletion or self-absorption problems. However, it was obviously not high enough to allow precise measurement of an absorption profile for comparison with the fluorescence results. The normalized fluorescence profile is shown in Fig. 3. The error limits for the fluorescence data displayed in Figs. 2 and 3 are one standard deviation for the relative measurements, including the error in temperatures. The absorption calibration measurement for NH had 25% error limits.<sup>1</sup> The fractional error in each absolute data point is thus  $[(0.25)^2 + (\Delta R/R)^2]^{1/2}$  where R represents the relative concentration and  $\Delta R$  its error from Fig. 3. The absolute error limits for OH concentrations resulting from fluorescence measurements must be treated in a similar fashion using the data of Fig. 2.

In addition to the concentration measurements on NH and OH, the NH equilibrium was checked by running an R-branch excitation scan in the (0,0) band in a manner entirely similar to previous scans on OH. The monochromator settings were the same as those mentioned previously. Obviously some improvement in this experiment might be achieved by setting the monochromator on the Q-head, but quite adequate results were obtained for our purposes. The resulting spectrum is shown in Fig. 4. This spectrum is similar to the (0,0) band spectrum observed in a flow system in Ref. 20. All of the (0,0) band transitions observed in Ref. 20 were readily identified in the flame. In addition, approximately forty (1,1) band R-branch transitions, including all of the main branch R triplets for N = 4 to 16, were readily identified in the flame and assigned using the analyses of Funke<sup>24</sup>. The (1,1) band transitions undoubtedly occur

<sup>23</sup> Anderson, W.R., Decker, L.J. and Kotlar, A.J., "Measurement of OH and NH Concentration Profiles in Stoichiometric CH<sub>4</sub>/N<sub>2</sub>O Flames by Laser Excited Fluorescence," paper 67, Eastern Section Fall Meeting of the Combustion Institute, Princeton, New Jersey, November, 1980.

<sup>24</sup> a. Funke, G.W., "Die NH Banden bei  $\lambda 3360$ ," *Zeit. Physik*, Vol. 96, p. 51, 1935. b. Funke, G.W., "Das Absorptionsspektrum des NH," *Zeit. Physik*, Vol. 101, p. 104, 1936.

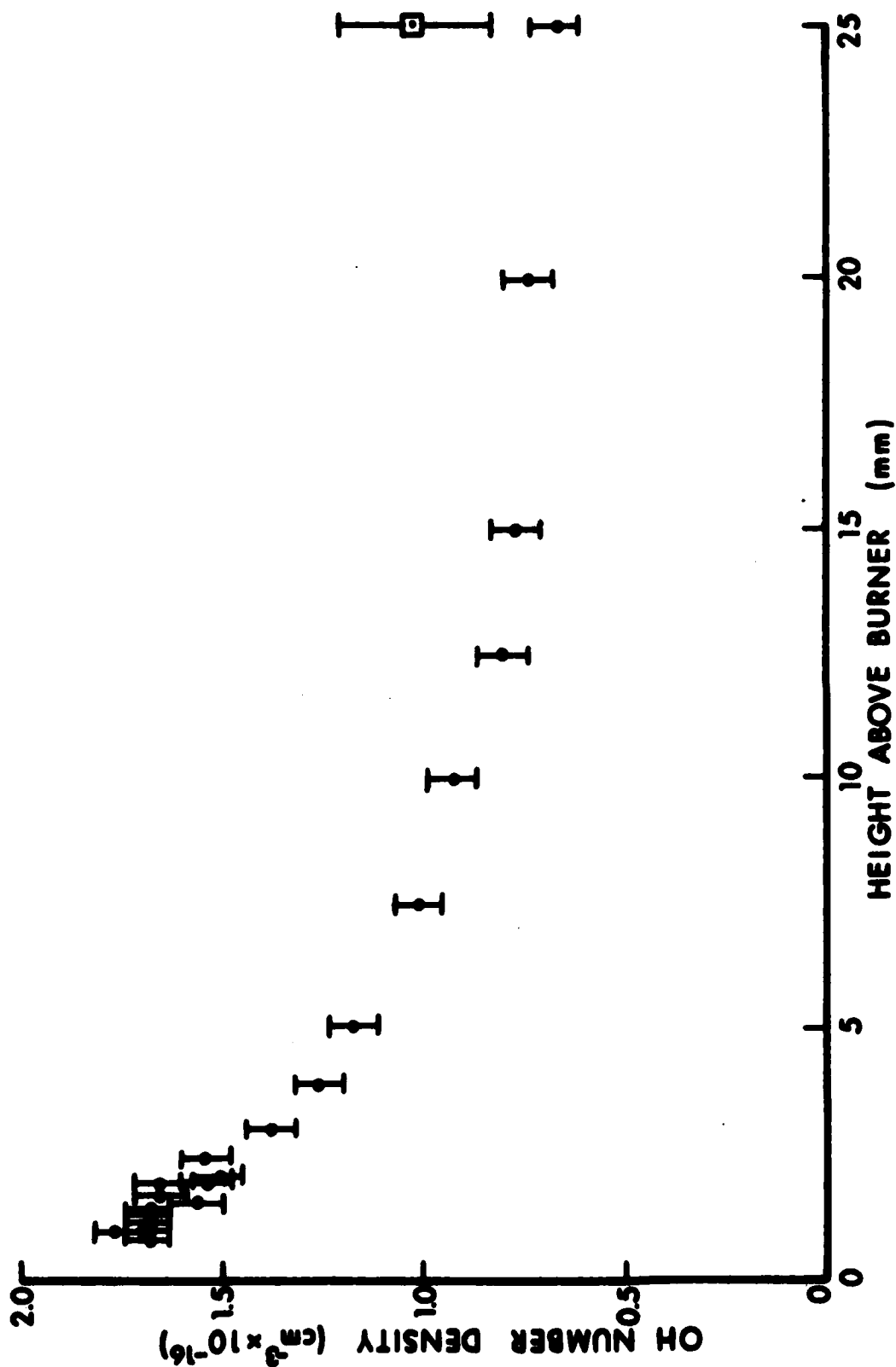


Fig. 2. OH profile in stoichiometric CH<sub>4</sub>/N<sub>2</sub>O flame. Only relative error limits are shown for the fluorescence measurements. Absolute error limits are shown for absorption measurements. Some systematic error may also be present in the absorption results because of the line of sight nature of the measurements. See Text.

2a. Decay of the OH in the burnt gas region. The points result from fluorescence measurements normalized to absorption measurements as discussed in the text. The open square at the right of the figure is the calculated equilibrium value. The error in this value arises from that in the temperature measurement.



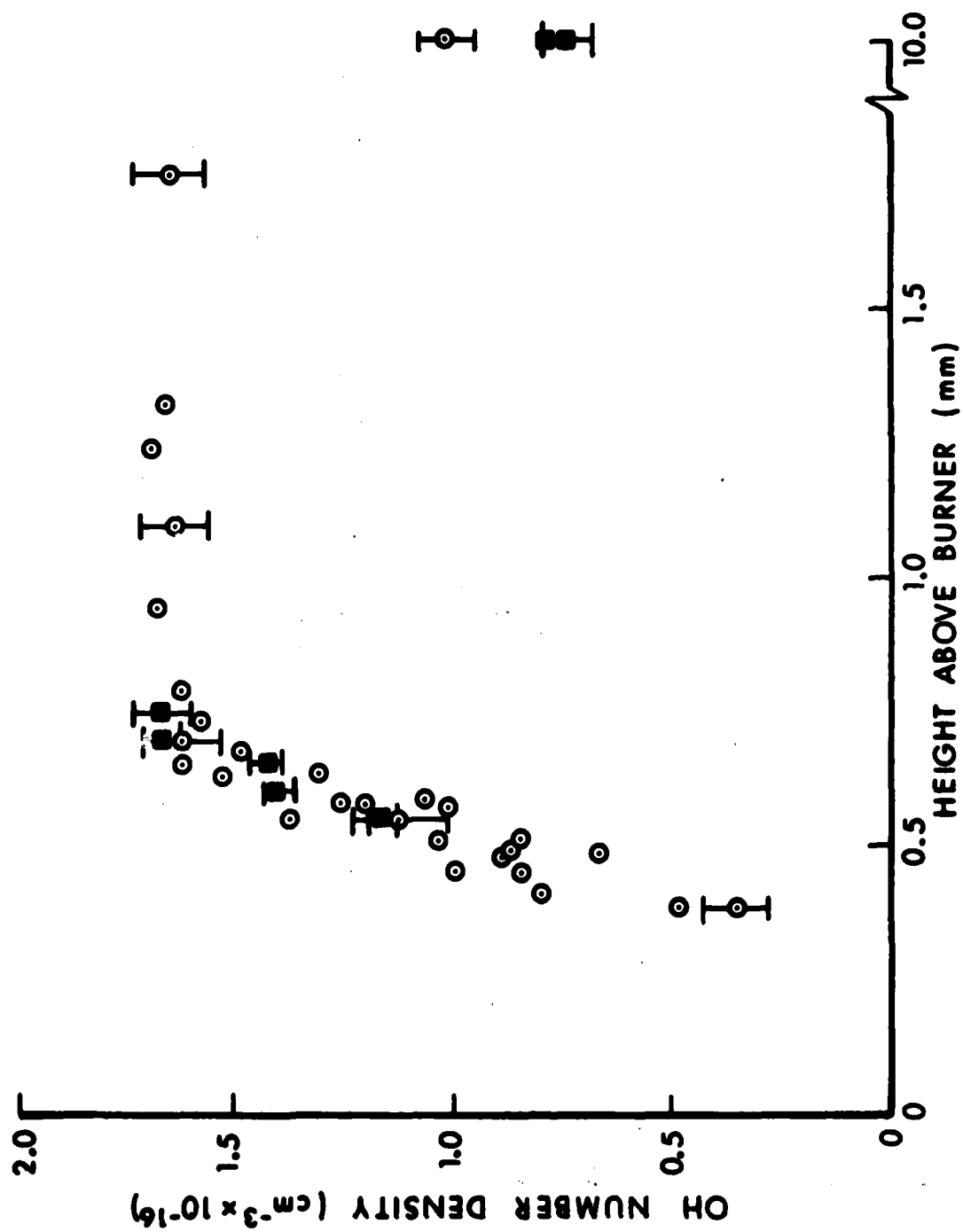


Fig. 2b. Growth profile in flame front. Open circles - fluorescence results. Closed squares - absorption results.

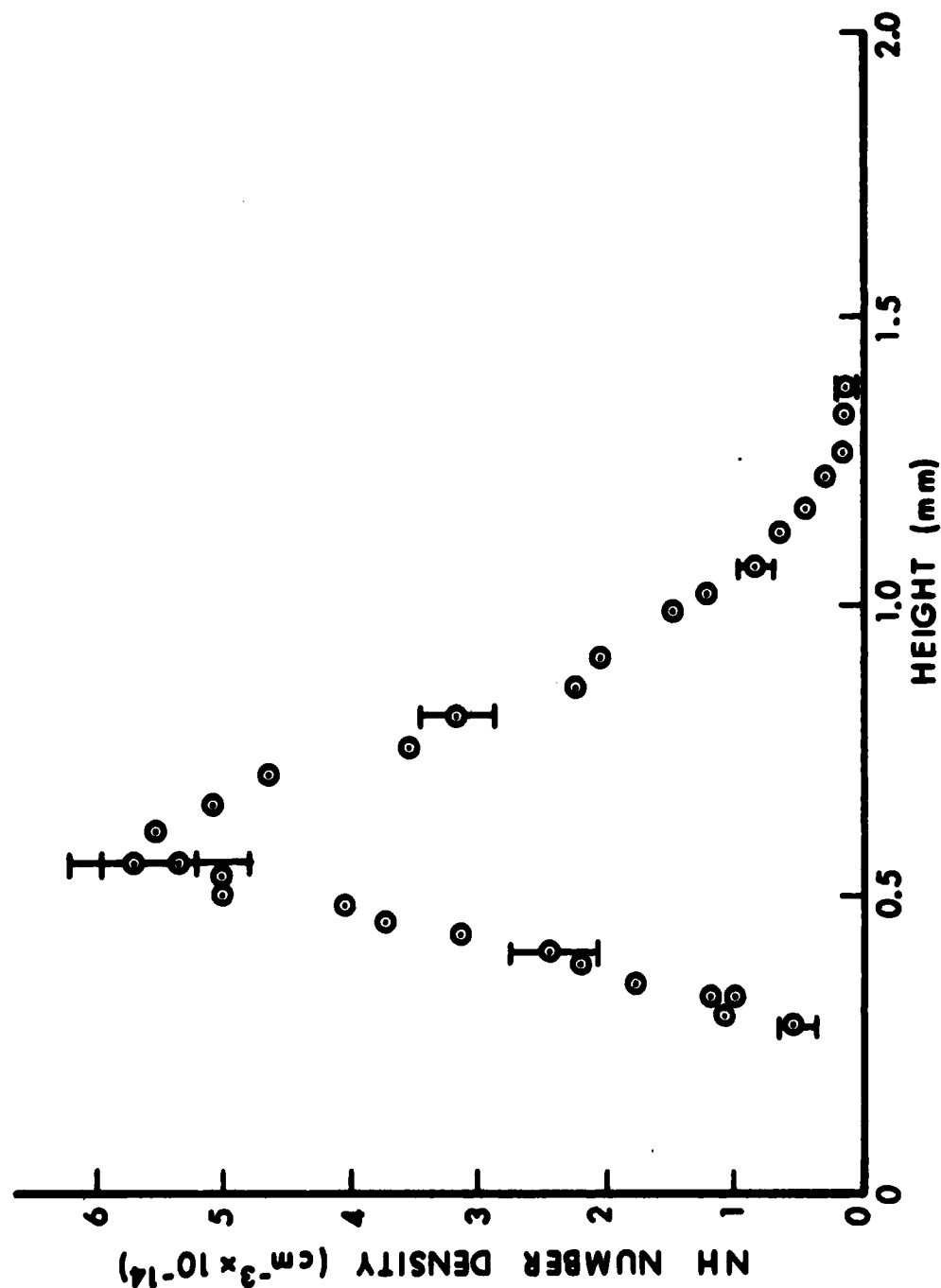


Fig. 3. NH profile in stoichiometric  $\text{CH}_4/\text{N}_2\text{O}$  flame. The fluorescence profile was normalized by an absorption measurement at approximately 0.55 mm. Only relative error limits are shown. An additional 25% error must be included in the error propagation to obtain the absolute error limits.

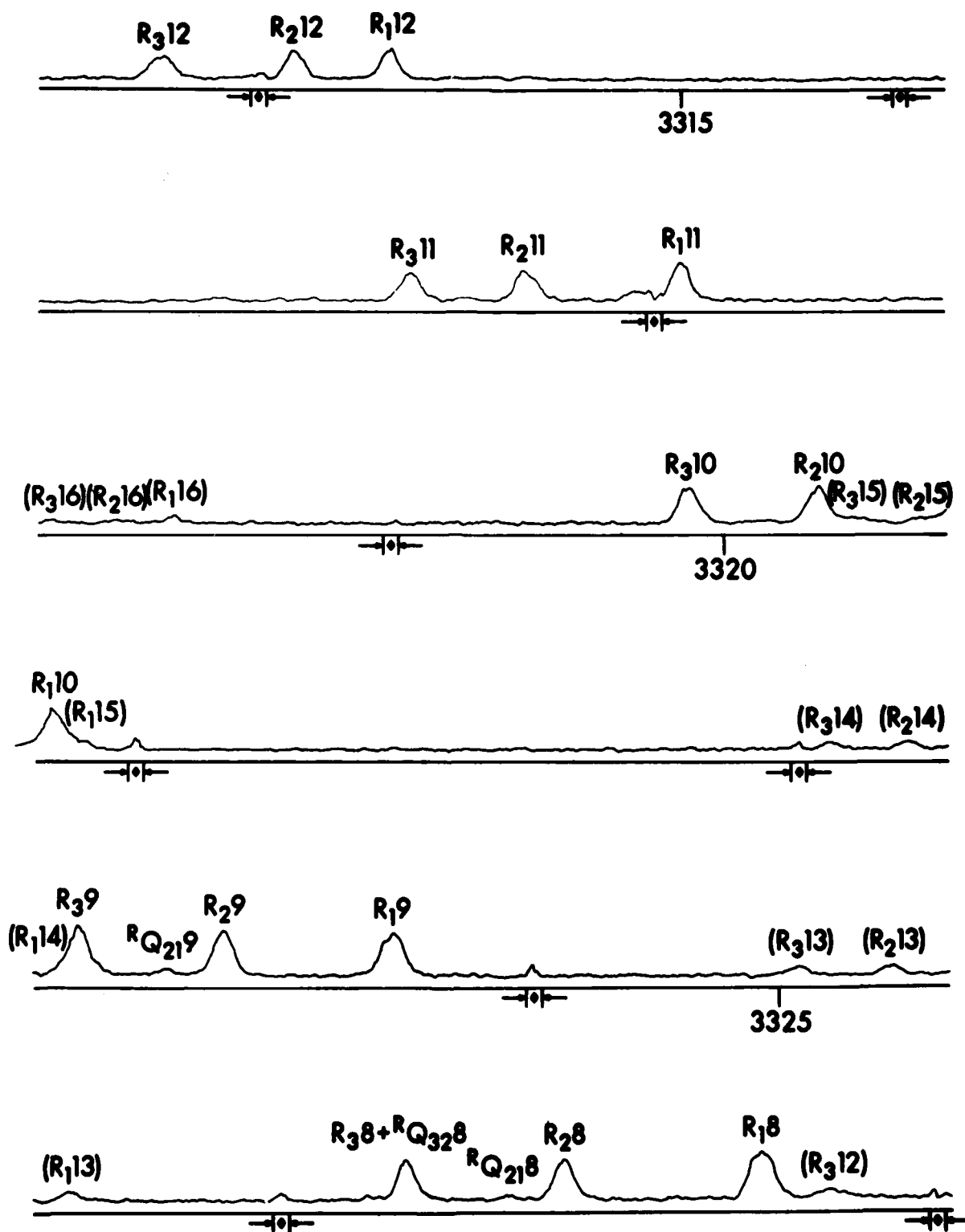
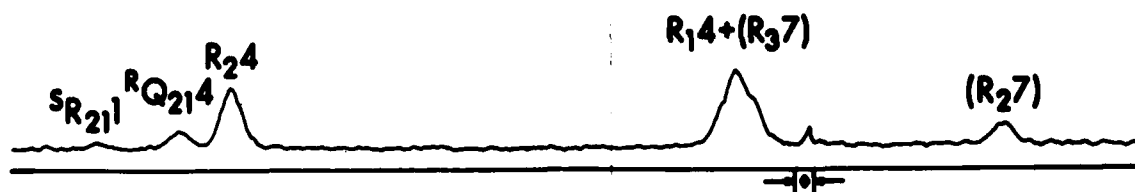
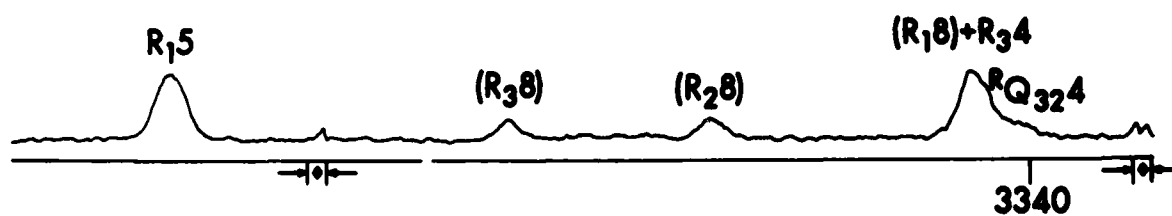
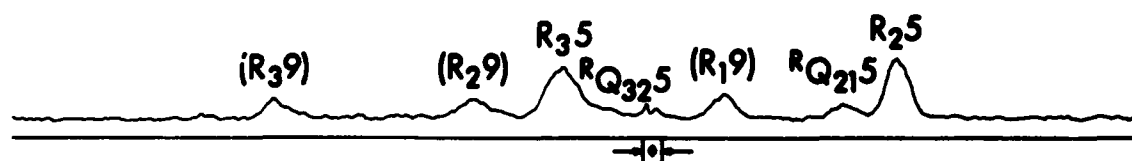
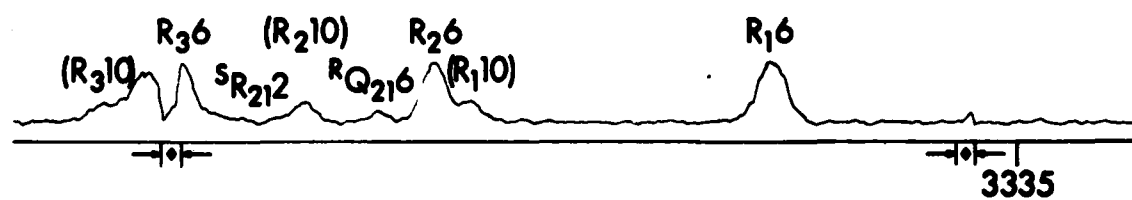
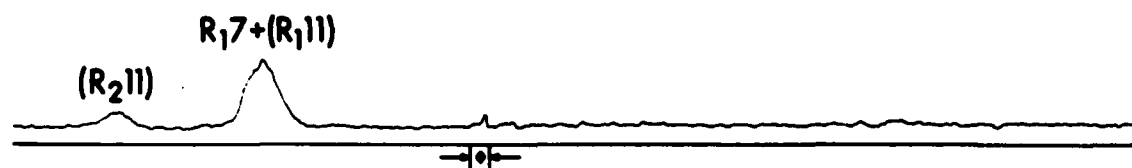
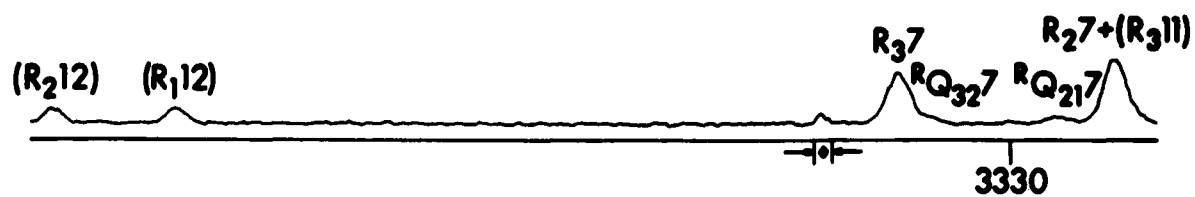
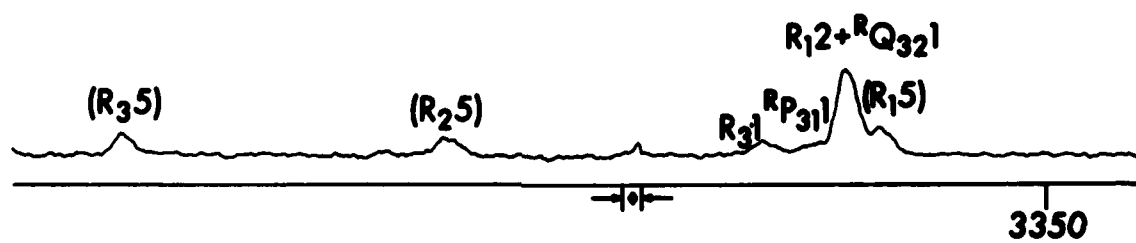
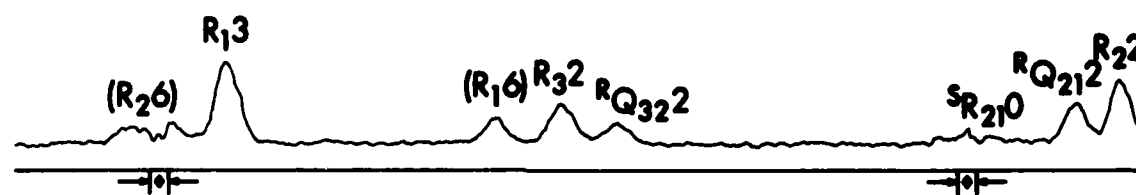


Fig. 4. NH R-branch excitation scan. Designations without parentheses - (0,0) band, with parentheses - (1,1) band. Wavelengths in angstroms. Diamonds enclosed in arrows indicate points where the laser's internal etalon was reset.





because of much hotter temperatures in the flame vs. the flow system leading to an appreciable  $v'' = 1$  population.

The (0,0) band intensities were analyzed by making the assumption that the intensity is proportional to the laser pumping rate and the ground state is equilibrated, as was done for OH in Ref. 7. These assumptions lead to the equation

$$\ln [I/B_{N'',J''}(2J'' + 1)] = -E_{N'',J''}/kT + C \quad (3)$$

where  $I$  is the normalized fluorescence intensity and  $B_{N'',J''}$  is the Einstein coefficient for the appropriate transition. The fluorescence lifetimes are nearly the same (within 1%) for all of the rotational states studied.<sup>25</sup> Furthermore, greater than 99% of the transition probability from  $v' = 0$  to the  $X^2\Sigma^-$  state is to states with  $v'' = 0$ .<sup>20</sup> In such a case, it can be shown that the  $B_{N'',J''}$  are proportional (within a minor wavelength dependence) to the Honl-London rotational overlap factors divided by the ground state degeneracy, i.e.  $S_{J'',J'}/(2J''+1)$ . The  $S_{J'',J'}$  were obtained from the calculation of Ref. 26. The resulting plot of Eq. 3 for NH is shown in Fig. 5. The plot obviously only becomes a straight line for high-lying rotational levels. This result is undoubtedly because of rotational energy transfer effects and biasing of the detector bandpass towards transitions connected to the lower energy levels. The effect was discussed in more detail in regards to OH thermometry in Ref. 7. Nevertheless, the temperature thus measured,  $2210 \pm 120K$ , is in reasonable agreement with a (1,1) band measurement on OH at the same point in the flame,  $0.539 \pm 0.002$  mm above the burner, yielding  $2040 \pm 120K$ .

#### IV. DISCUSSION

##### A. Laser Fluorescence Diagnostics

As can be seen from Fig. 2b, the agreement between OH concentration profiles resulting from absorption and fluorescence measurements is quite good, even well into the flame front. The agreement was not anticipated since the quench rate, and thus the fluorescence efficiency, was expected to change in the flame front. The result suggests the quench rate is instead nearly constant in the flame as was observed by Cottureau and Stepowski<sup>13</sup> in low pressure  $C_3H_8/O_2$  flames. Raman measurements of major species concentration and temperature by Bechtel and Teets led to similar results for atmospheric pressure  $CH_4$ /air flames<sup>12</sup>. Observations of a nearly constant quench rate for OH in the present work lend credence to the shape of the NH profile for which absorption measurements were not possible. Studies to indicate under what conditions the quench rate is constant would be quite useful.

<sup>25</sup> Smith, W.M., Brzozowski, J. and Erman, P., "Lifetime Studies of the NH Molecule: New Predissociations, the Dissociation Energy, and Interstellar Diatomic Recombination," *J. Chem. Phys.*, Vol. 64, p. 4628, 1976.

<sup>26</sup> Luoh, R.P., Peterson, R.C. and Laurendeau, N.M., "Fundamentals of Absorption Spectroscopy for Selected Diatomic Flame Radicals," *Purdue University Report No. PURDU-CL-78-06*, October, 1978.

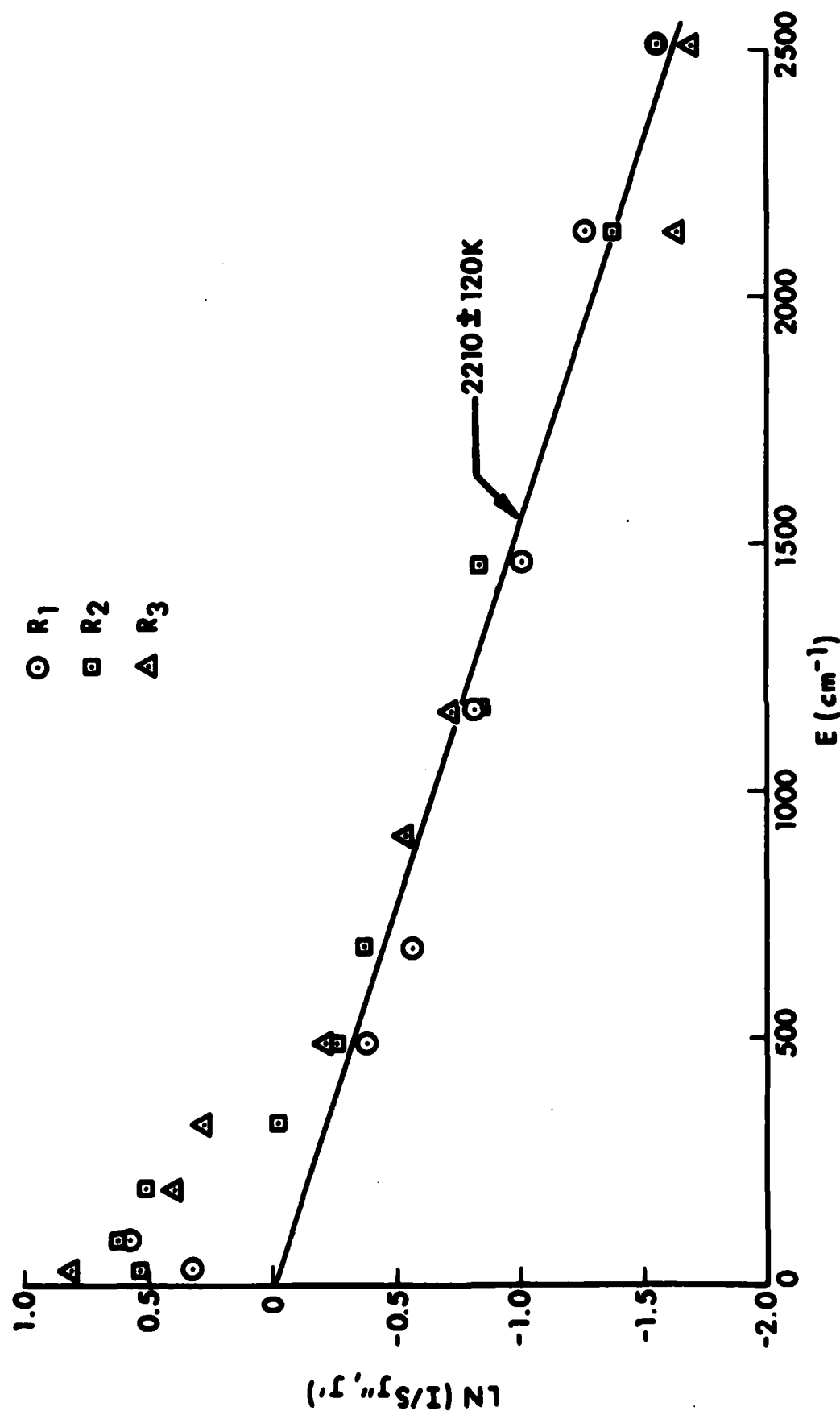


Fig. 5. Boltzmann plot for several NH (0,0) band R-branch transitions. The line is a least squares fit to points with  $E$  greater than or equal to  $489 \text{ cm}^{-1}$ . Exclusion of the three points at  $489 \text{ cm}^{-1}$  reduces the precision of the fit, but does not change the result appreciably.

Also shown in Fig. 2 is the equilibrium concentration of OH at the measured final flame temperature, 2200K<sup>7</sup>. The concentration was calculated by constraining the NASA thermodynamic equilibrium computer code<sup>27</sup> to the observed final temperature using our starting fuel mixture. Error bars in this quantity resulted almost entirely from the error in the measured temperature. Though the calculated concentration is somewhat higher than observed and does not agree within error limits (even when the absorption calibration error is considered), the agreement is quite good for this type of absolute measurement. The difference may be partially because of the nonconstant horizontal OH profile in the flame observed in Ref. 7. There, a slightly lower concentration was observed over the center of the burner than at the edge. The NH equilibrium concentration at 2200K is several orders of magnitude below the peak concentration in Fig. 3, and is below the sensitivity of our experimental arrangement.

Since the completion of our experiments, NH laser excited fluorescence has been used for measurements of concentration and temperature in NH<sub>3</sub>/O<sub>2</sub>/Ar flames<sup>28</sup>. The experimental approach was similar to ours. Preliminary results show the temperatures from excitation scans are in good agreement with measurements by other methods, as our work indicated.

#### B. CH<sub>4</sub>/N<sub>2</sub>O Flame

Measurements of the concentrations of OH and NH in all of the flames studied will be discussed in this section with emphasis on the flame chemistry. The discussion will be primarily directed towards the N<sub>2</sub>O-supported flames, especially the CH<sub>4</sub> flame.

An examination of the radical profiles in Figs. 2 and 3 reveals several interesting features. Perhaps the most obvious is that the NH is confined to the flame front whereas the OH decay extends well into the burnt gas region. Also, the onset of formation of the two radicals appears at the same point in the flame, ~ 250μ above the burner head. It is interesting to note that the luminous zone of the flame starts ~ 250-300μ above the surface and is about 0.3-1.0 mm wide.\* The sharp decay of the NH profile indicates that it is consumed in a bimolecular reaction, which is not unexpected owing to its high reactivity, and also that reactions forming NH are no longer important. On the other hand, the OH decay, which is much slower, results from three body recombinations of radicals in the burnt gases. Such decays were studied by Bulewicz, James and Sugden<sup>14</sup>, Kaskan<sup>15</sup> and Fenimore and Jones<sup>17</sup> in flames and by Getzinger and Schott<sup>18</sup> in a shock tube for various mixtures of H<sub>2</sub>, O<sub>2</sub> and inert diluents. It was found that H and O atoms and OH radicals were in partial equilibrium in the burnt gas region, with H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O as buffer gases; and the decay in flames exhibited apparent second order kinetics in the OH concentration. This type of behavior was also confirmed by Egorov, Ermolenko and Ryabikov<sup>16</sup> and by Cattolica<sup>9</sup> for the OH decay in CH<sub>4</sub>/air flames of varying stoichiometry. In addition, Cattolica reduced the data of Lück<sup>8c</sup> for CH<sub>4</sub>/air

\*Distances were measured using a cathetometer. The width is difficult to measure owing to problems in determining the upper boundary of the luminous zone.

<sup>27</sup> Svehla, R.A. and McBride, B.J., "Fortran IV Computer Program for Calculation of Thermodynamic and Transport Properties of Complex Chemical Systems" NASA TN D-7056, 1973, (1981 program version).

<sup>28</sup> Bechtel, J.H., private communication.

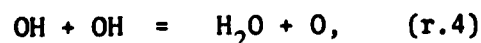
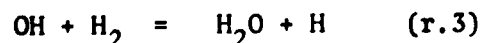
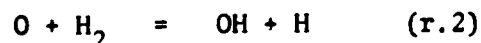
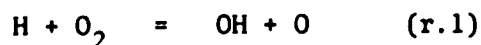


flames showing that it, too, supports the apparent second order decay. The influence of radical diffusion was pointed out in the study of Cattolica by comparison of models with and without transport effects taken into account. The diffusion can, and in many flames probably does, change the shape of the OH profile, making the radical decay appear to be second order in the OH concentration.

The apparent second order decay mechanism is examined here for the stoichiometric  $\text{CH}_4/\text{N}_2\text{O}$  flame. For a reaction second order in OH, a plot of  $[\text{OH}]^{-1}$  vs. time, which is proportional to height, should be linear with a slope equal to the reaction rate constant. Such a plot for the profile in Fig. 2a is shown in Fig. 6. The plot is linear within error limits until the last two points where the equilibrium concentration is approached and back reactions apparently become important. The result thus has the appearance of a second order decay. The flow rate in the burnt gas region was calculated from the known fuel flow rates, burner cross section, temperature ratio<sup>7</sup>, and fuel : product mole ratio, ignoring minor burnt gas components.\* The burnt gas flow rate was used to convert the slope in Fig. 6 to a decay rate constant. The result is  $3.49 \pm 0.34 \times 10^{-15} \text{ cm}^3/\text{sec}$ . This rate constant must be divided by the total number density of the flame to yield a third order rate constant which may be compared to results for  $\text{CH}_4/\text{air}$  flames. The resulting rate constant,  $1.05 \pm .11 \times 10^{-33} \text{ cm}^6/\text{sec}$ , is about a factor of 5 smaller than any of the previous results for stoichiometric  $\text{CH}_4/\text{air}$  flames<sup>8c,9,16</sup>. This result is at first somewhat surprising when one considers that the burnt gas regions of these stoichiometric flames are quite similar in major species composition. It was later noted that the OH decay rate constant monotonically increases as the final flame temperature decreases for a given equivalence ratio  $\phi$ . (Final flame temperatures for the  $\text{CH}_4/\text{air}$  flames were not the same presumably because of differences in burner design and its influence on cooling rates). The present result for  $\phi = 1.01$   $\text{CH}_4/\text{N}_2\text{O}$  follows the trend of the  $\text{CH}_4/\text{air}$  data. The final flame temperature of 2200K measured for  $\text{CH}_4/\text{N}_2\text{O}$  on our burner is about 130K higher than the highest measured  $\text{CH}_4/\text{air}$  temperature.

The same type of trend with temperature was found for rich and lean conditions by examining results of the three  $\text{CH}_4/\text{air}$  experiments<sup>8c,9,16</sup>. Models which quantitatively predict this trend for rich and lean flames were presented by Kaskan<sup>15</sup>. The stoichiometric flames are more difficult to model. Detailed qualitative arguments which show this trend is to be expected for the stoichiometric flames as well are presented in the next several paragraphs.

Examination of the mechanism presented in Refs. 14,15,17, and 18 for  $\text{H}_2/\text{O}_2$  inert diluent flames indicates that the reactions



which cannot lead to radical recombination and overall equilibration of the system, are very fast in comparison to the recombination reactions and are assumed to remain in partial equilibrium throughout the decay region. The radical decay is likely due to some combination of the reactions

\* Use of the thermodynamic equilibrium code<sup>27</sup> indicates there is less than 1% dissociation at the measured flame temperature of 2200 K.

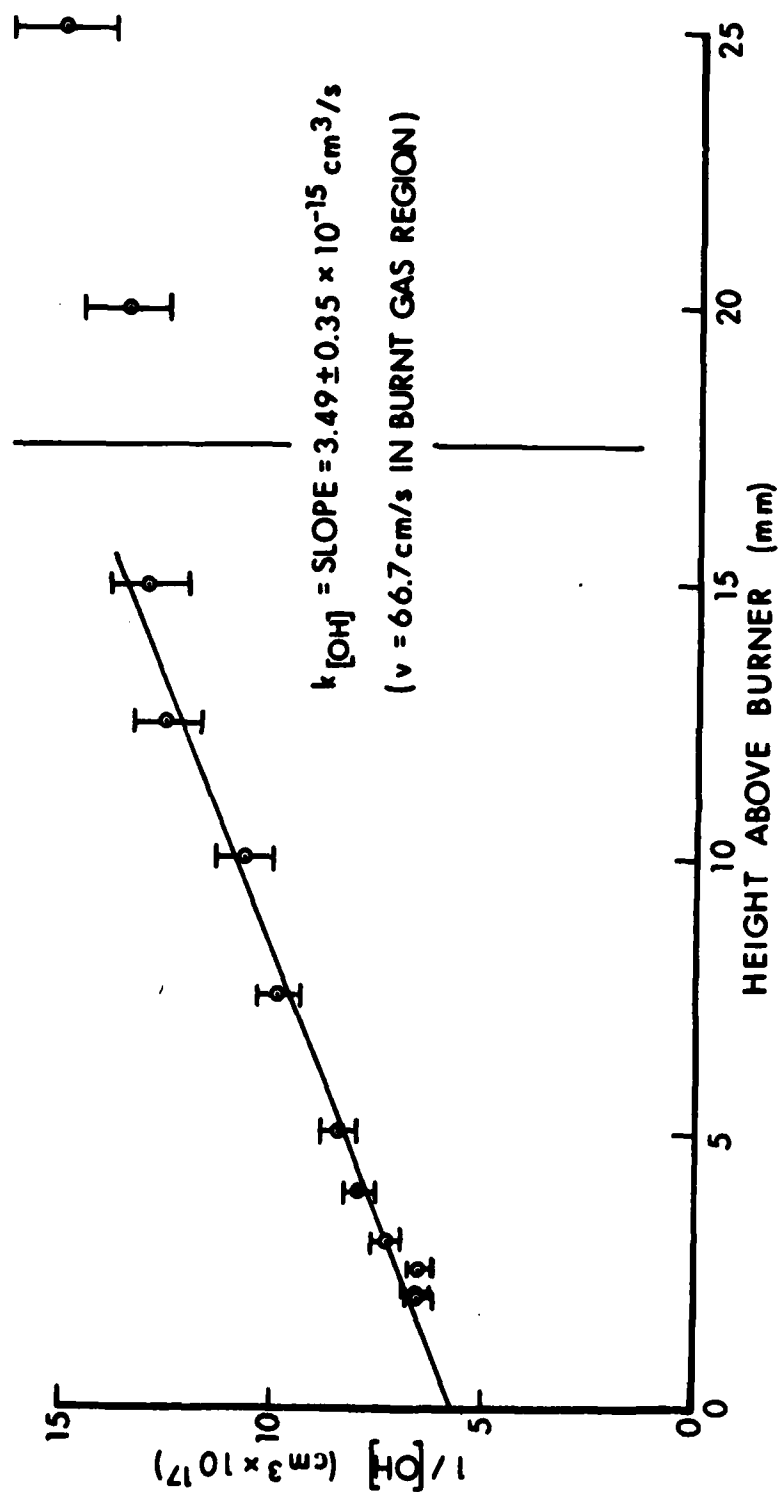
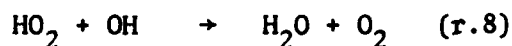
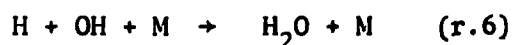
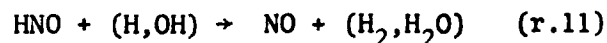


Fig. 6. Determination of the apparent second order OH decay rate constant in the burnt gas region of the  $\text{CH}_4/\text{N}_2\text{O}$  flame. Points to the right of the vertical line are not included in the least squares fit. Back reactions apparently become important at this height.



where arrows indicate the reverse reaction is negligible. In rich flames r.5 and r.6 dominate, while in lean flames r.7 followed by r.8 is most important. The decay mechanism in  $\text{CH}_4/\text{N}_2\text{O}$  flames should be similar to that in  $\text{H}_2/\text{O}_2/\text{inert}$  diluent flames provided reactions involving CO and NO, the two additional non-inert products present in the burnt gases in appreciable quantity, are not important. CO should not be important because its principle reaction, oxidation by OH, leads to production of H which simply reequilibrates via r.1 - r.4. NO could catalyze the recombination via a sequence such as



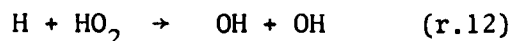
which has been discussed extensively in connection with nitrogen oxide flame chemistry in a recent review by Dixon-Lewis and Williams<sup>29</sup>. The decay mechanism in  $\text{CH}_4/\text{air}$  flames is also expected to be similar to that in  $\text{H}_2/\text{O}_2/\text{inert}$  diluent flames since CO is the only additional noninert product present in the burnt gases in appreciable quantity. Mass spectrometric<sup>30</sup> and absorption and emission studies<sup>31</sup> indicate presence of NO at the level of several percent in the burnt gases of  $\text{N}_2\text{O}$  supported flames, while another mass spectrometric study<sup>4</sup> indicates the concentration of NO is much lower in the burnt gases of  $\text{CH}_4/\text{air}$  flames. (Odor of the burnt gases would seem to support this result). Reactions r.10 and r.11 are highly exothermic as written. The sequence r.10 - r.11 can, therefore, only increase the radical decay rate in  $\text{N}_2\text{O}$  supported flames in comparison to air supported flames. Thus, it cannot explain the observed lower OH decay rate of the  $\text{CH}_4/\text{N}_2\text{O}$  flame.

<sup>29</sup> Dixon-Lewis, G. and Williams, D.J., "The Oxidation of Hydrogen and Carbon Monoxide," in *Comprehensive Chemical Kinetics*, (Bamford, C.H. and Tipper, C.F.H., Eds.), Elsevier Scientific Publishing Company, New York, 1977, Vol. 17, p. 1.

<sup>30</sup> Balakhine, V.P., Vandooren, J. and Van Tiggelen, P.J., "Reaction Mechanism and Rate Constants in Lean Hydrogen-Nitrous Oxide Flames," *Combustion and Flame*, Vol. 28, p. 165, 1977.

<sup>31</sup> a. Gaydon, A.G. and Wolfhard, H.G., "Spectroscopic Studies of Low-Pressure Flames," *Third Symposium (Int.) on Combustion*, Williams and Wilkins, Baltimore, 1949, p. 504. b. Parker, W.G. and Wolfhard, H.G., "Some Characteristics of Flames Supported by NO and NO<sub>2</sub>," *Fourth Symposium (Int.) on Combustion*, Williams and Wilkins, Baltimore, 1953, p. 420. c. Wolfhard, H.G. and Parker, W.G., "Spectra and Combustion Mechanism of Flames Supported by the Oxides of Nitrogen," *Fifth Symposium (Int.) on Combustion*, Reinhold, New York, 1955, p. 178. d. Hall, A.R., McCoubrey, J.C. and Wolfhard, H.G., "Some Properties of Formaldehyde Flames," *Combustion and Flame*, Vol. 1, p. 53, 1957.

In order to examine the validity of the partial equilibrium assumption and the relative importance of the various recombination reactions, a flame model developed by Coffee and Heimerl<sup>32</sup>, which includes both a complex chemical kinetics set and physical transport properties such as diffusion, was run for rich, lean and stoichiometric H<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> flames of about the same adiabatic flame temperature, ~ 2100K. The model predicts reactions r.1 - r.4 are approximately equilibrated in the recombination region. The three body recombination reactions are in general much slower than any other reactions of importance in the burnt gas region, especially reactions r.1 - r.4 which equilibrate O, H and OH with H<sub>2</sub> and H<sub>2</sub>O. The major recombination reactions in rich and lean flames were those mentioned previously, as expected. For the stoichiometric flame, the reaction



competes strongly with r.8, thus reforming radicals and reducing the importance of r.7 in the recombination mechanism. It appears that r.6 is somewhat more important in this case. Still, r.7 may retain some influence on the recombination. Thus, some combination of r.6 and r.7 is rate controlling for the radical recombination in the stoichiometric flame. Now, one notes that H<sub>2</sub>O is much more important as a chaperone molecule than any other in the burnt gas region of the flame<sup>29</sup>. Therefore, one may write  $[M] \approx [\text{H}_2\text{O}]$  and use the appropriate rate constants in r.5 - r.7 for  $M = \text{H}_2\text{O}$ . Using the equilibrium relations for r.1 - r.4, the following reaction rates are then found for reactions r.6 and r.7, respectively,

$$R_6 \approx k_6 K_4 [\text{OH}]^4 / K_1 [\text{O}_2] \quad (4)$$

$$R_7 \approx k_7 K_4 [\text{OH}]^5 / K_1 \quad (5)$$

where the  $k_i$ 's represent forward rate constants and the  $K_i$ 's equilibrium constants. Now,  $d[\text{OH}]/dt$  is not directly proportional to these rates for any flame due to the equilibrium in r.1 - r.4. It is the radical pool, which is a combination of polynomials in O, H and OH concentrations, whose decay rate is described by some combination of these rates. (See Ref. 15a for a discussion of the radical pool concept and its use in determining a simple closed form solution for the OH concentration vs. time for rich flames. Such a simple solution is not possible for lean<sup>9,15b</sup> or stoichiometric flames). The OH decay is expected to follow the radical pool decay monotonically. The OH decay clearly is not chemically second order in OH. The diffusion in the flame probably accounts for the good fit to second order rate laws. Nonetheless, since  $d[\text{OH}]/dt$  is expected to follow some combination of  $R_6$  and  $R_7$  monotonically, Eq. 4 and 5 can be used to gain some qualitative insight concerning the relative OH decay rates in

<sup>32</sup> a. Coffee, T.P. and Heimerl, J.M., "A Method for Computing the Flame Speed of a Laminar, Premixed, One Dimensional Flame," BRL Technical Report ARBRL-TR-02212, January 1980, AD-A082803. b. Coffee, T.P., "A Computer Code for the Solution of the Equations Governing a Laminar, Premixed, One Dimensional Flame," BRL Memorandum Report, ARBRL-MR-03165, April 1982. (AD A114041)

various flames whose recombination chemistry is similar to that in  $\text{H}_2/\text{O}_2/\text{inert}$  diluent flames. Since the  $\text{CH}_4/\text{N}_2\text{O}$  and  $\text{CH}_4/\text{air}$  flames probably involve similar chemistry, as discussed previously, Eq. 4 and 5 may now be used to investigate their comparative decay rates. We will first concentrate on a comparison between our  $\text{CH}_4/\text{N}_2\text{O}$  flame and Cattolica's stoichiometric  $\text{CH}_4/\text{air}$  flame<sup>9</sup> whose measured temperature was  $2000 \pm 100\text{K}$ . We will then compare these with the other results<sup>8c,16</sup>. The effective rate constant for r.7 is  $k_7 K_4 / K_1$ . This quantity is approximately 2.5 times larger at 2000K than at 2200K.\* The effective rate constant for r.6 is  $k_6 K_4 / K_1 [\text{O}_2]$ . The quantity  $k_6 K_4 / K_1$  is also approximately 2.5 times higher at 2000K than at 2200K. (In both cases this results mainly because of shifts in  $K_1$  and  $K_4$ .  $k_6$  and  $k_7$  only decrease by about 10% at the higher temperature). At the measured temperatures the computed equilibrium concentration of  $\text{O}_2$  in Cattolica's stoichiometric  $\text{CH}_4/\text{air}$  flame is about 0.16 mole percent while for the  $\text{CH}_4/\text{N}_2\text{O}$  flame it is about 0.56 mole percent. If the ratio of these concentrations is representative of that throughout the burnt gas region of both flames, one expects the effective rate constant would, therefore, be more than 2.5 times larger for Cattolica's flame for r.7. Thus, both effective rate constants are larger for Cattolica's flame. In addition, the measured peak OH concentration for Cattolica's  $\text{CH}_4/\text{air}$  flame is approximately 1.5 times that reported here for the  $\text{CH}_4/\text{N}_2\text{O}$  flame. The higher OH concentration and rate constants in the  $\text{CH}_4/\text{air}$  flame combine to make  $R_6$  and  $R_7$  larger there than in the  $\text{CH}_4/\text{N}_2\text{O}$  flame. The mechanism thus agrees, qualitatively, with the observed results.

The studies of Lück<sup>8c</sup> and Egorov, Ermolenko and Ryabikov<sup>16</sup> are in reasonably good qualitative agreement with the preceding interpretation for the OH decay mechanism. Cattolica<sup>9</sup> reports results from his data reduction of Lück's decay profiles. In general, the decay rates from Lück's work, measured as a function of equivalence ratio  $\phi$ , are slightly lower than those measured by Cattolica. In particular, the decay rate for the stoichiometric  $\text{CH}_4/\text{air}$  flame falls between that measured by Cattolica for  $\text{CH}_4/\text{air}$  and that from the present study on  $\text{CH}_4/\text{N}_2\text{O}$ . This result is particularly encouraging since the measured temperatures of Lück's flames were generally  $\sim 100\text{K}$  higher than Cattolica's flame of nearly the same equivalence ratio. For the stoichiometric flame the final temperature was, of course,  $\sim 100\text{K}$  lower than for the  $\text{CH}_4/\text{N}_2\text{O}$  flame of the present study. The magnitude of the effective rate constants for  $R_6$  and  $R_7$  thus fall between those for Cattolica's and the present study leading to the observed results for the decay rates. Egorov, Ermolenko and Ryabikov measured decay rates for a rich, lean and nearly stoichiometric flame,  $\phi = 1.20, 0.75$  and  $1.02$ , respectively. The resulting decay rates were much higher than those measured by Cattolica, Lück or in the present work. The rates are approximately a factor of 50 higher than Cattolica's rates for flames of similar equivalence ratios. The measured flame temperatures were approximately 450K lower than the adiabatic flame temperatures for the mixtures chosen ( $\sim 200\text{K}$  lower than in Cattolica's work). The result thus fits the trend expected for lean and stoichiometric flames. However, Cattolica points out that if Kaskan's interpretation for rich flames<sup>15a</sup> (which is based on a subset of the reactions presented here applicable to rich flames and which assumes partial equilibrium of r.1 - r.3) is correct, then the resulting decay rate for Egorov, et al's  $\phi = 1.23$  flame

\* Estimates for  $k_6$  and  $k_7$  were obtained from Ref. 29.

should be only a factor of  $\sim 2$  higher than for Cattolica's comparable  $\phi = 1.20$  flame. Cattolica at first speculated that the observed high recombination rate may somehow be due to a measured  $[H]/[OH]$  ratio much higher than the equilibrium value for  $r.3$  at the measured flame temperature, that is, a breakdown of the partial equilibrium assumption. The high ratio was pointed out by Egorov, Ermolenko and Ryabihov in comparing their results on OH with earlier work on H atoms by Ryabihov and coworkers<sup>33a</sup>. However, two points should be made about these results and their interpretation. First, the calculated equilibrium concentration of OH for Egorov, et al's  $\phi = 1.02$  flame is a factor of 4 higher than the result at the furthest distance from the burner. At this point ( $\sim 10$  msec or 1 cm above the burner) the OH concentration is probably still falling so that their result for the equilibrium OH concentration would have been even smaller if it had been measured. A similar statement holds for the lean  $\phi = 0.75$  flame except the factor is at least six. For the rich  $\phi = 1.23$  flame, the concentration measured at the furthest point from the burner was only 10% lower than the equilibrium calculation, but again the concentration still appears to be falling. The results of Cattolica and Luck for their stoichiometric flames yield concentration factors of 3 and 2, respectively, above the calculated equilibrium concentration for their temperatures. In addition, the concentrations appear to be falling and approach the equilibrium concentration, though not so closely as in the present work. Thus, it would appear the OH concentration in  $CH_4$ /air does, in fact, approach its equilibrium value in the burnt gases, as one would expect. To strengthen this argument, we also noted that the results of Ref. 16 indicate the OH concentration first rises above its equilibrium value in the flame front before dropping well below this value in the burnt gases. Therefore, one cannot argue that source reactions are too slow to produce the equilibrium concentration. There is, therefore, serious doubt as to the quantitative validity of the results of Egorov, et al for the lean and stoichiometric flames and quite possibly the rich one as well. If the OH concentrations are low by a systematic multiplicative error, which could happen in any of a number of ways, the recombination rates for the  $\phi = 0.75$  and  $1.02$  flames are reduced by factors of at least 6 and 4, respectively. The results would still be in good qualitative agreement with the mechanism discussed in the present study. If the result for the  $\phi = 1.23$  flame is similarly affected, the true decay rate would be much closer to the value one would expect relative to the measurements of Luck and Cattolica using Kaskan's model. The rate constants of Ref. 16 need to be remeasured before they can be used to conclusively prove anything. This has been done for one case in Ref. 2. The results indicate the original measurements of concentration<sup>16</sup> were indeed quite low as we suspect.

The second point mentioned above concerns the burners used in the studies of Ryabihov and coworkers<sup>16,33a</sup>. The burners used for the H atom and OH measurements were of different construction. The burner used for the OH work was a sintered porous plug type, quite similar to the present study. That used for the H atom work was a simple quartz tube, 6 mm in diameter, into which the pre-mixed gases were fed. The latter burner is described, in Ryabihov and coworker's

<sup>33</sup> a Gussak, L.A., Ryabihov, O.B., Politenkova, G.G. and Furman, G.A., "Mechanism and Kinetics of Intermediate Product Formation in an Auxiliary Mixture and Their Effect on the Combustion Process in a Working Mixture," *Doklady Akademii Nauk SSSR*, Vol. 208, p. 1126, 1973.

earlier paper on the use of ESR to measure H atom concentrations in  $H_2/O_2/N_2$  flames.<sup>33b</sup> The latter type of burner clearly does not produce a one-dimensional flat-flame, as does the porous plug burner. Also, tube burners typically extract less heat, particularly at the center of the flame, than the porous plug type, so the flame temperature reached is probably much higher. In addition, the flow rates and dimensions of the burners used in the experiments lead to vertical gas velocities of  $2.21 \text{ l/cm}^2\text{-min}$  for the quartz tube burner, but only  $0.255 \text{ l/cm}^2\text{-min}$  for the porous plug type burner. Both factors would lead one to expect the concentration of atomic and radical species to be much higher for the quartz tube than the porous plug burner. It is, therefore, not surprising that the  $[H]/[OH]$  ratio reported by Ryabihov and coworkers was so large. It is difficult, if not impossible, to determine the quantitative meaning of the result.

Before leaving this subject, a word of caution concerning the aforementioned analysis should be noted. A comparison of a stirred reactor model and a model containing detailed chemical and physical effects by Cattolica<sup>2,9</sup> led to the conclusion that diffusion of OH in the decay region is quite important and can even change the apparent order of the recombination. Also, the chemistry even in the decay region is quite complex making it difficult to predict to what extent reactions r.5 - r.7 are important in a given flame. And, though the  $H_2/O_2/N_2$  flame model predicts r.1 - r.4 are close to equilibrium, they were not quite equilibrated. Systematic shifts of  $\sim 10\text{-}15\%$  in the concentration ratios for r.1 - r.4 away from their equilibrium values at the appropriate temperatures were noted at all points in the predicted concentration profiles. Thus, though interesting comparisons can be drawn, as was done here, a detailed model will be necessary to quantitatively understand and interpret the results.

The high concentration of NH observed in these studies is worth some comment. The observed peak concentration is several orders of magnitude higher than the equilibrium concentration. Measurements of the NH concentration of a much less precise nature than for the  $CH_4/N_2O$  flame were performed for stoichiometric  $CH_4/\text{air}$  (flow rate  $22 \text{ l/min}$  at  $298\text{K}$ ) and  $H_2/N_2O$  (flow rate  $16 \text{ l/min}$  at  $298\text{K}$ ) flames and for  $CH_4/NO$  and  $H_2/NO$  flames of unmeasured stoichiometry. Several mixtures ranging from lean to rich were tried for the latter two flames. The rate of heat removal by the burner head, inferred from the inlet and outlet water temperatures, indicates there is little cooling of the  $CH_4/\text{air}$  flame while heat removal for  $H_2/N_2O$  is nearly the same as for  $CH_4/N_2O$  which was  $10.6 \pm 1.0 \text{ kcal/min}$ .<sup>7</sup> Heat removal for the NO-supported flames was not measured. From these results, one concludes the final flame temperatures of the  $CH_4/\text{air}$ ,  $CH_4/N_2O$  and  $H_2/N_2O$  flames are all nearly the same on the porous-plug burner. The NH peak concentration in the  $H_2/N_2O$  flame, measured by absorption with factor of two error limits because of the lack of a precise temperature measurement, is the same as the peak concentration in the  $CH_4/N_2O$  flame. In addition, the peak occurs at nearly the same height above the burner. No NH fluorescence could be found in the  $CH_4/\text{air}$ ,  $CH_4/NO$  or  $H_2/NO$  flames with sensitivity limits of  $\sim 5 \times 10^{12} \text{ cm}^{-3}$  which is a factor of 100 lower than the peak concentration in the  $N_2O$ -supported flames. The results for the  $CH_4/\text{air}$  and  $H_2/NO$  flames are in good agreement with previous emission studies<sup>314</sup>

<sup>33b</sup> Samoilov, I.B., Ryabihov, O.B., Zaichikov, V.V., Gershenson, Yu. M. and Gussak, L.A., "Investigation of the Combustion of Hydrogen-Air Mixtures at Atmospheric Pressure by the ESR Method," *Doklady Akademii Nauk SSSR*, Vol. 205, p. 1138, 1972, English, 703.

where little NH emission was observed. In one of the previous emission studies<sup>31c</sup>, some absorption experiments were performed as well. Atmospheric pressure flames were set up in the necessary configuration to perform line reversal temperature measurements with a carbon arc light source. The NH 3360 Å band never appeared in absorption for hydrocarbon/NO flames in spite of the fact that the temperature of the carbon arc is typically 3800K, which is much higher than the adiabatic flame temperatures of these flames. In fact, the NH and CH bands were readily observed in emission in the C<sub>2</sub>H<sub>2</sub>/NO flame with the carbon arc background. The previous and present work thus suggest the presence of strong NH chemiluminescence in hydrocarbon/NO flames.

Presence of NH in the N<sub>2</sub>O-supported flames can only occur if the N-N bond of the N<sub>2</sub>O is in some way broken to form N atoms or single N-atom molecules. Lack of appreciable NH signal in the CH<sub>4</sub>/air flame excludes N<sub>2</sub> decomposition, unimolecular or otherwise, as the source of compounds containing only one N atom in the N<sub>2</sub>O flames. One may also argue that unimolecular decay of N<sub>2</sub>O to NO + N is not responsible since the N-N bond is much too strong (~ 115 kcal/mole). By elimination, one is therefore led to the conclusion that some bimolecular reaction is responsible for the N-N bond breakage in the N<sub>2</sub>O supported flames. Furthermore, it is apparent from the H<sub>2</sub>/N<sub>2</sub>O study that the carbon containing compounds might not be at all important in breaking this bond. Since comparable amounts of NH are formed in both H<sub>2</sub>/N<sub>2</sub>O and CH<sub>4</sub>/N<sub>2</sub>O flames, one is tempted to infer that a similar mechanism based on non-carbon containing compounds holds for each. Lack of NH emission or laser excited fluorescence in the H<sub>2</sub>/NO flame would seem to rule out reactions of NO as an indirect source of the NH. One other possibility is the reaction of H and N<sub>2</sub>O. The channel leading to NH + NO has been inferred, indirectly, to be over a factor of 100 slower than that to OH + N<sub>2</sub> at temperatures of 540 and 600°C.<sup>34</sup> Of course, this channel could become more important at higher temperatures. A direct study of the H + N<sub>2</sub>O branching ratio would be most helpful. At present, this reaction appears to be the most promising explanation for formation of NH in the flame.

The reaction of H<sub>2</sub> with N<sub>2</sub>O has been reviewed recently by Dixon-Lewis and Williams (Ref. 29, p. 158-165). In this review it is suggested that NH reacts with N<sub>2</sub>O to form HNO. (Rate constants for this reaction were unknown). It was also suggested that HNO may react with H or OH in chain termination steps, inhibiting the flame. It is thus possible that formation of trace amounts of NH eventually leads to inhibition of N<sub>2</sub>O-supported flames. Clearly, measurements of NH + N<sub>2</sub>O reaction rate constants and of HNO concentrations in flames are desirable for evaluating this possibility.

## V. CONCLUSION

The ability to measure NH and OH concentration profiles in the reaction zone of a flame over a flat-flame, porous-plug burner at atmospheric pressure by laser excited fluorescence is clearly demonstrated by this work. Profiles of these compounds were measured in a CH<sub>4</sub>/N<sub>2</sub>O flame. Comparison of the OH profiles

<sup>34</sup> Baldwin, R.R., Gethin, A., Plaistow, J. and Walker, R.W., "Reaction Between Hydrogen and Nitrous Oxide," *J. Chem. Soc. Faraday Trans. I*, Vol. 71, p. 1265, 1975.



from fluorescence and absorption data leads to the conclusion that changes in the fluorescence quench rate do not occur in the regions of interest in the flame in agreement with previous studies on  $C_3H_8/O_2$  flames<sup>13</sup> and  $CH_4$ /air flames.<sup>12</sup> The NH in the  $N_2O$ -supported flames was confined to the flame front region. Cruder measurements of an upper limit on the NH concentration in air- and NO-supported flames point toward a major difference in the nitrogen chemistry in these flames. Much more work in profiling of nitrogen containing compounds in these flames remains to be done before a full understanding of their chemistry will be possible.

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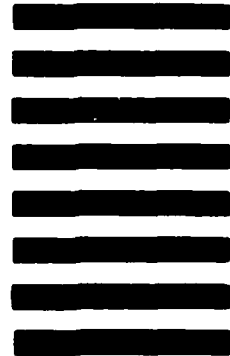


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